

CALCIUM DEACTIVATION IN CO₂ AND STEAM GASIFICATION REACTIONS

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INTRODUCTION

Catalytic activity loss during the gasification reaction has a great practical importance. The factors controlling the deactivation process are difficult to study due to the difficulty of fixing all the variables related with the catalytic activity and to the lack of a simple technique able to evaluate "in situ" the changes undergone by the catalyst during the reaction.

In this sense the deactivation of a gasification catalyst has not been extensively investigated and is, without appropriate experimental support, generally related to (1,2): a) the mineral matter content of the carbon, b) the available internal surface area of the carbon, c) the catalyst addition method and d) the catalyst nature.

Currently it is well accepted that calcium is a good catalyst for the carbon-gas reactions (3) but deactivates more severely than potassium (4). These results were interpreted owing to inability of calcium species to redisperse themselves as occurs with potassium species. However results obtained in lignites with ion-exchanged calcium (3,5-7) do not seem to have so great tendency to deactivate. To interpret the different results found in the literature (mainly caused by the different experimental conditions used, as well as, by the nature of the gasification agents and of the carbon studied), it will be helpful to develop a simple experimental technique able to follow the catalyst modifications over the gasification reaction.

Recently, a "in situ" CO₂ chemisorption technique has been used to determine the active area of CaO particles in a carbon-CaO system, in order to interpret the carbon-gas reactions (8,9). This technique will be applied, together with X-ray diffraction, to analyse the calcium deactivation process during the carbon gasification reaction. The following factors have been studied: a) initial catalyst dispersion, b) reaction temperature and c) reaction agents. In order to simplify the study, the carbon used has almost no impurities and has a large surface area and a highly accessible porosity, to minimize their effects.

EXPERIMENTAL

A phenolformaldehyde resin has been treated in N₂ flow (5 K/min to 1273 K, 1h) to prepare the carbon used for this study.

To increase its calcium exchange capacity, the carbon has been oxidized in 15N HNO₃ solution (1 g of carbon/10 ml solution) at 353 K to dryness and washed until free of nitrate ions.

Calcium has been loaded by ion-exchange from a 1.5M calcium acetate solution (7 g of carbon/50 ml solution); calcium loading obtained is 3.2 wt %. The contact time of the ion exchange (from 10 min to 8 h) do not significantly change the wt % calcium uptake.

Carbon reactivities (CO₂ and steam) and CO₂ chemisorption at 573 K has been studied following the thermogravimetrically (STA-780) experimental procedures described elsewhere (9,10).

RESULTS AND DISCUSSION:

Figure 1 presents CO₂ reactivities at 1073 K (0.1 MPa) of four samples with different activation degrees obtained by treatment of the original sample -0 % burn-off in the Figure- in CO₂ at 1073 K during different reaction time. Reactivity decreases noticeably with gasification time. Taking into account that reactivity increases lightly with burn-off for the uncatalyzed samples (8), it seems reasonable to ascribe the reactivity loss to changes occurring in the catalyst over the gasification reaction.

X-ray diffraction patterns for these samples are shown in Fig. 2. There is no evidence of calcium species for the original sample (0 % burn-off) whereas CaCO₃ reflection peaks are obtained for the reacted samples in CO₂ (samples were cooled in CO₂ atmosphere before XRD study). The absence of detectable crystallites in the unreacted sample which is not caused by the small wt % calcium used (CaCO₃ reflection peaks has been observed in a narrow porosity carbon using lower wt % of calcium loading), is indicative of a high calcium dispersion in the carbon matrix; its particle size should be lower than the XRD technique detection limit. With increasing gasification level the peaks sharpen; there is an increase in crystallite size owing to an enlargement of the catalyst particles. This increase in particle size should be the responsible of the deactivation process observed in Figure 1.

CO₂ chemisorption technique at 573 K (8,9), during 30 min, has been applied to the calcium/carbon samples, after been heat treated in N₂ (20 K/min) up to 1173 K (10 min). Heat treatment decomposes the ion-exchanged calcium (in the case of the unreacted sample) and the CaCO₃ (in the reacted samples) to CaO. The amount of CO₂ chemisorbed is related to the CaO present at the surface of the CaO particles.

In Table 1 are compiled, for comparison purposes, the average size of the CaO particles obtained by X-ray diffraction and CO₂ chemisorption. Both techniques clearly show an enlargement of particle size during the gasification reaction. X-ray diffraction does not allow to deduce the particle size of the unreacted samples and gives significantly larger values than chemisorption. This happens because XRD has a non-detectable particle range <5 nm which

displaces the average particle size to higher values. Consequently XRD technique will be severely limited in a catalyzed gasification reaction, considering that the main catalytic activity is due to these very small particles. Furthermore XRD technique can not be applied "in situ" to the TG reactor, as it has been done with CO_2 chemisorption.

From Figure 3, where the CO_2 reactivity data are plotted versus the CaO average particle size, deduced by chemisorption, it is evident that reactivity is function of the catalyst particle size. Gasification reaction causes a noticeable reduction of the catalyst surface area exposed to the reaction atmosphere -by an enlargement of its particle size- and therefore a catalytic activity loss is observed with increasing the activation degree.

Effect of initial catalyst dispersion

The effect that the initial catalyst dispersion has on the reactivity and on its deactivation behaviour over the reaction time has been studied. The calcium/carbon sample has been heat treated in N_2 up to 1223 K during two hours in order to modify its initial dispersion. Figure 4 and 5 show respectively, the evolutions of the CO_2 reactivities at 1023 K and of the CaO surface areas, versus the activation degree for both the original and heat treated sample.

Reactivities have been calculated from one simple TG experiment and are expressed per gram of the initial weight of the carbon used. CaO surface areas are obtained in the TG reactor with samples partially reacted in CO_2 in the TG system.

Heat treatment causes a noticeable decrease in reactivity (comparable to that obtained during the reaction in CO_2 after a 40 % activation degree) as well as a change in the reactivity evolution profile.

Figure 5 has a very good parallelism with Figure 4 indicating the close relation between catalytic reactivity and available surface area of the catalyst. In that sense it is noteworthy to point out that the heat treatment causes a 50 % reduction in both the initial reactivity and the CaO surface area.

The different reactivity behaviours, of the original and heat treated sample, versus activation degree can be related to a different sintering process caused by the heat treatment. After 20 % burn-off there is for the treated sample a much lower deactivation process than for the original sample.

Effect of reaction temperature

Figures 6 and 7 show respectively CO_2 reactivity (at 1023 and 1073 K) and CaO dispersion (obtained from CO_2 chemisorption), plotted versus the activation degree. Again it is important to recall the shape similarity of these two figures which corroborates the catalytic activity and the CaO dispersion relationship. The

reactivity loss is higher the higher is the reaction temperature used owing to a greater sintering process.

It is interesting to note in Figure 7 that the initial dispersions (for samples with 0 % burn-off) at 1023 and 1073 K, are not the same. The reason is that CaCO_3 formation is much favoured at 1023 K than at 1073 K, as it has been checked by XRD and TG-DTA technique (8). There is an instantaneous decrease in calcium dispersion when CO_2 is introduced in the reactor at 1023 K before the activation process starts. CaCO_3 favours the sintering process respect to CaO .

A closer look to Figures 6 and 7 shows that decreasing the reaction temperature reactivity decreases in a factor of 3 (burn-off degree <20 %), while CaO surface area only decreases in a factor of 1.5. These results seems to make clear that besides the importance of the catalyst dispersion there is an additional effect caused by the chemical changes in the catalyst due to the different reaction temperatures used. For a given temperature, the rate changes in reactivity, are very similar to the rate change observed in the dispersion degree as also happened in Figs. 4 and 5.

Effect of reaction atmosphere

Calcium catalytic activity has been studied in CO_2 (0.1 MPa) and in steam (19.7 KPa) at 1073 K. Figure 8 and 9 show respectively reactivity and CaO surface area results versus reaction time. Figure 8 clearly reveals that calcium activity is much higher in CO_2 than in steam under the experimental condition used. It is noteworthy that during gasification in steam the catalyst keeps a constant activity in contrast with the behaviour observed in CO_2 atmosphere. Reactivity results are confirmed and become evident from the changes observed in the catalyst surface area, as a function of the reaction atmosphere, in Figure 9. In steam no appreciable change in the catalyst surface area is observed. The burn-off degrees obtained in both reactions, after reaction time of 20 and 80 min, for CO_2 and steam respectively, are comparable.

Considering that both reactions have been studied at the same reaction temperature, it is evident that the gas phase atmospheres, as well as the different partial pressures used affect the chemical composition of the catalyst and its sintering behaviour. In CO_2 atmosphere (0.1 MPa) the catalyst is very active and the reaction mechanism involves a transformation of the active specie (probably CaO) to CaCO_3 , as it has been proved by XRD. The CaCO_3 shows a promoted sintering behaviour due to the higher CO_2 partial pressure in the system. However in steam (19.7 KPa), where the catalyst activity is quite smaller, there is no evidence of a complet transformation of the active phase to carbonate because of the CO_2 partial pressure is very low. The calcium species present under the steam gasification will be: mainly CaO , some Ca(OH)_2 (which will decompose to CaO) and a small amount of CaCO_3 . The lower tendency of CaO respect to CaCO_3 to sinter is evident from Figure 9 as it is also expected from the Tamman

Temperature (1501 and 838 K respectively).

CONCLUSIONS

A polymer carbon of high purity, high surface area and easy accessibility to the porous structure provides a simple medium to study the calcium deactivation during gasification reactions in CO₂ and steam.

XRD technique has severe limitations to be applied in the study of catalyzed carbon gasification. The range of undetected particles sizes are expected to be the most actives in the gasification reactions. CO₂ chemisorption technique is able to measure the specific surface area of the active calcium species, without need to take the sample out of the reactor.

Catalyst deactivation during the reaction is a direct consequence of a loss in active surface area (or enlargement of the particle size). Heat treatment, reaction gas and reaction temperature have a remarkable importance in the calcium deactivation process. Reactivity results for the different factors studied are closely related to CO₂ chemisorption data.

BIBLIOGRAPHY

- (1) Van Heek, H.K. and Muhlen, H.J., Fuel 64 1045 (1985).
- (2) Moulijn, J.A. and Kapteijn, F. "Carbon and coal gasification" Eds. J.L. Figueiredo and J.A. Moulijn, 181 (1986).
- (3) Linares Solano, A., Hippo, E.H. and Walker, P.L.Jr., Fuel 65 776 (1986).
- (4) Kapteijn, F., Pore, H. and Moulijn, J.A., AIChE Journal, 32 691 (1986).
- (5) Radovic, L.R., Walker, P.L.Jr. and Jenkins, R.G. J. Catal. 82 382 (1983).
- (6) Hippo, E.J., Jenkins, R.G. and Walker, P.L.Jr., Fuel 58 338 (1979).
- (7) Walker P.L.Jr., Matsumoso, S., Hanzawa, T., Miura, T. and Ismail, I.M.K., Fuel 62 140 (1983).
- (8) Alameda Alarcón, M., PhD. Thesis. University of Alicante. (1988).
- (9) Linares Solano, A., Salinas Martínez de Lecea, C. and Almela Alarcón, M., ICCS 559. Elsevier Science Publishers (1987).
- (10) Fernandez González, C., Linares Solano, A., McEnaney, B. and Salinas Martínez de Lecea, C., Fuel 65 991 (1986).

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Table 1

Average CaO particle size (nm)
by XRD and CO₂ chemisorption

X/burn-off	XRD	CO ₂
15	9	3.3
28	13	3.6
40	18	4.6

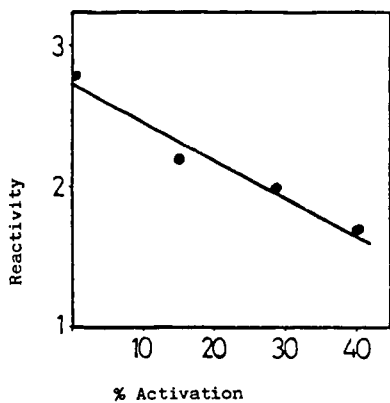


Figure 1. CO_2 Reactivity at 1073K versus degree of activation.

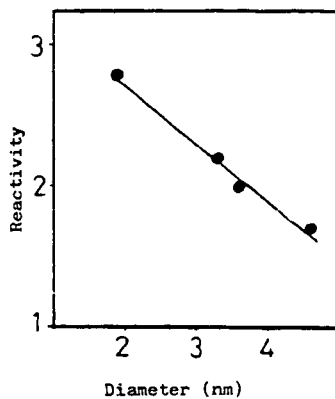


Figure 3. Reactivity versus CaO particle size.

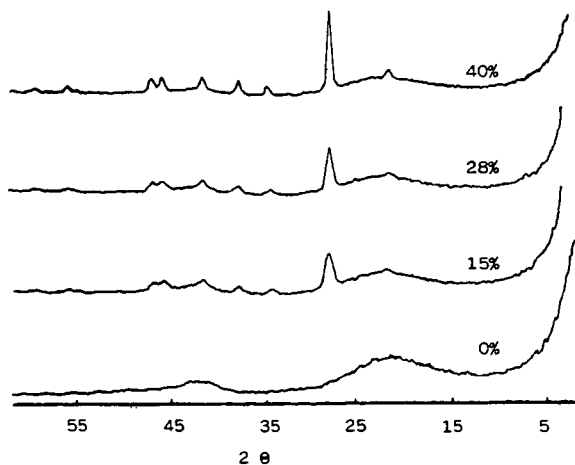


Figure 2. X-Ray diffraction profiles of samples with different degree of activation.

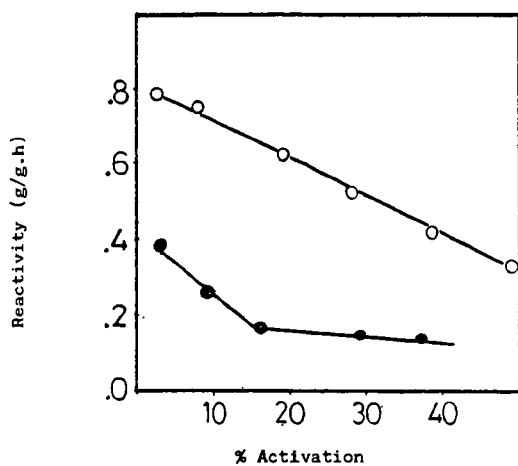


Figure 4. CO₂ Reactivity at 1023K versus degree of activation. (O) original sample, (●) heat treated sample.

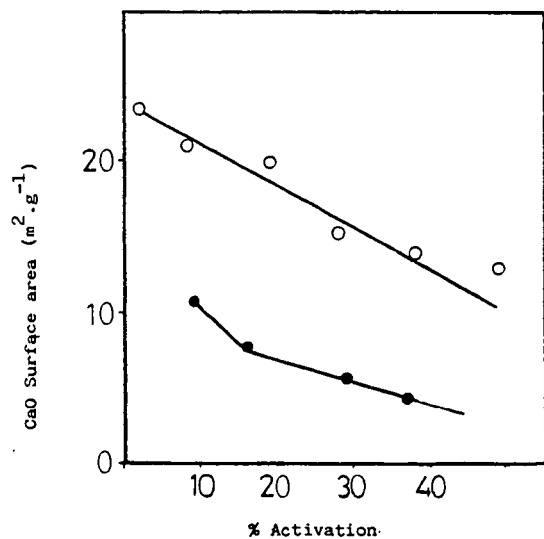


Figure 5. CaO surface area versus degree of activation. (O) original sample, (●) heat treated sample.

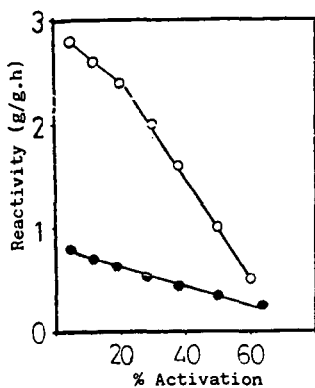


Figure 6.

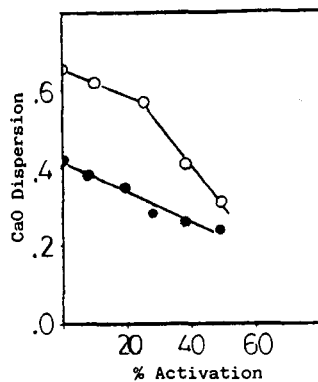


Figure 7.

Figure 6. CO₂ Reactivity versus degree of activation.

○ 1073K, ● 1023K.

Figure 7. CaO Dispersion versus degree of activation.

○ 1073K, ● 1023K.

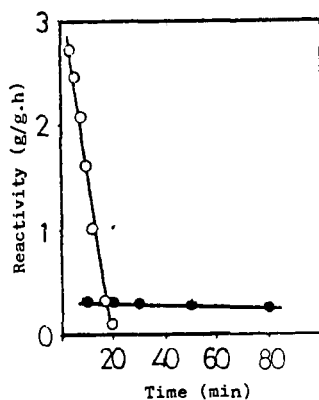


Figure 8.

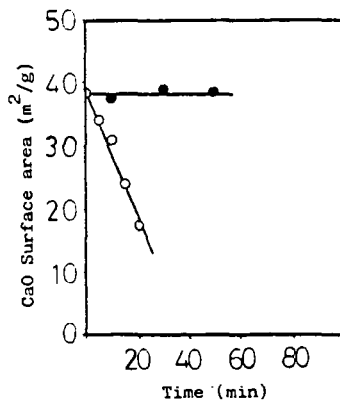


Figure 9.

Figure 8. Reactivity in CO₂ (○) and steam (●) at 1073K versus time of reaction.

Figure 9. CaO Surface area in CO₂ (○) and steam (●) versus time of reaction.